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Studies of polymer ball type polymer dispersed liquid crystal films

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Studies of polymer ball type polymer dispersed liquid crystal films

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'Reverse' or 'polymer ball' polymer dispersed liquid crystal (PDLC) samples were prepared by a photopolymerization induced phase separation method. A detailed study of the effects of the sample preparation parameters, such as curing time, curing intensity, and liquid crystal concentration are reported. It was found that by adjusting these parameters, we were able to change the morphology of these 'polymer ball' PDLC samples and thus change their optical characteristics. Incomplete polymerization of the PDLC samples results in a higher threshold voltage and a lower ON state transmission. When the amount of monomer is too low, the shape of the resulting polymer ball becomes irregular, and the sample has a larger threshold voltage and a larger saturation voltage.

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1. Introduction

In recent years, many studies have been devoted to the optical properties of polymer dispersed liquid crystal (PDLC) films [1–4]. Conventional PDLC films consist of liquid crystal droplets, having sizes of the order of micrometres, embedded in a transparent polymer matrix. By choosing appropriate combinations of liquid crystal and polymer material, the PDLC film can be optically switched with an electric field. PDLC systems exploit the anisotropic optical and dielectric properties of nematic liquid crystals to produce devices which change from a highly scattered or opaque state to a transparent state when a potential difference is applied across the film. The electro-optical switching behaviour is achieved by carefully matching the ordinary refractive index of the birefringent liquid crystal to that of the polymer. Such a PDLC light valve can be used for switchable windows and flat panel displays. Compared to conventional twisted nematic liquid crystal cells, PDLC cells are brighter, switch faster, have an improved viewing angle and are easily manufactured over large areas. A PDLC based, full colour thin-film-transistor-liquid-crystal-display (TFT-LCD) has also been demonstrated [5, 6].

Recently, a new kind of PDLC with a distinct type of polymer morphology, which is referred to as 'reversed' or 'polymer ball' morphology, has been reported [7–9]. Instead of forming microdroplets, the new type of PDLC films form narrower and irregular voids on crevices filled with the liquid crystal. The optical properties of the 'polymer ball' PDLC are also different from those of the 'droplet' PDLC. The 'polymer ball' PDLC has a memory effect in which a transparency is preserved for a long period of time after the applied electric field is removed. The transparent state can be erased and returned to the original opaque state by heating and cooling the film without applying an electric field. Using this memory effect, thermal addressed displays have successfully been realized [10–12]. However, only a few works have been reported on the properties of the 'polymer ball' PDLC films. Previously, Yamaguchi *et al.* [13], reported some preliminary results of the effects of curing time on the properties of the PDLC films. In order to have a better understanding of these films, we have performed a detailed study of this kind of 'polymer ball' PDLC films. In this paper, we report the effects of the sample preparation parameters, such as curing time, curing intensity, and liquid crystal concentration on the properties of the 'polymer ball' PDLC films.

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2. Experimental

The samples used in this study were prepared by the photopolymerization induced phase separation (PIPS) method. To synthesize the 'polymer ball' PDLC films, we used the UV curable 2-hydroxyethylmethacrylate (HEMA) as the monomer material, and a mixture of E7

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and K15 as the nematic liquid crystal material. The photoinitiator used in this study was 2,2-diethoxyacetophenone (DEAP). The mixture of monomer and liquid crystal, with a few weight percentage of photoinitiator, was then cured between two ITO-coated glass substrates. A UV lamp, HPA400/30S produced by Philips, with an output wavelength centred at 348 nm, was used for the curing process, and a UV photodetector G3641 was used to monitor the curing intensity. Samples synthesized at different curing times, curing intensities, and samples synthesized with different liquid crystal concentrations were prepared, and their opto-electrical properties were investigated. Scanning electron microscopy (SEM) was also used to study the microstructure of these films and to determine the size of the polymer balls.

To understand the opto-electrical properties of the synthesized 'polymer ball' PDLC films, we have studied their voltage–transmission characteristics. In this experiment, a He–Ne laser was used as the light source and a photodiode S/N211 and 4 photometer UDT380S were used for detection. In some cases, a neutral density filter was used to avoid saturation of the photodiode. The applied voltage across the sample was a square wave with a frequency of 200 Hz.

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3. Results and discussions

3.1. *Samples prepared with different curing times*

In this experiment, we first mixed the liquid crystal (E7 and K15) and monomer (HEMA) at a fixed ratio of E7:K15 = 1:1 and HEMA:(E7 + K15) = 1:1. The photoinitiator (DEAP) concentration was 5·36 % wt. Three samples were synthesized by curing the mixture at a constant UV intensity of 3 mW cm^{-2} but with different curing times (3 min, 15 min and 30 min). The film thickness was 12 μm for all three samples.

Figure 1 shows the voltage–transmission characteristics of the three samples. The filled symbols represent the ON state and the open symbols represent the memory state. It can be seen that samples cured with a longer curing time have a larger optical transmission in the ON state (filled symbols). For the memory state (open symbols), this difference is more obvious where the sample with the 3 min curing time shows almost no memory characteristics. As shown in figure 1, a longer curing time also lowers the threshold voltage.

Figures 2 (*a*), (*b*) and (*c*) show the SEM pictures of the three samples cured for 3 min, 15 min and 30 min, respectively. As shown in figure 2 (*a*), it can be seen that the shape of the polymer balls is irregular for the sample cured for 3 min. This is probably due to incomplete polymerization in this sample. For samples that were not completely polymerized, some liquid crystal monomers will remain. In such a case, the refractive index of the liquid crystal will be changed and the ON state

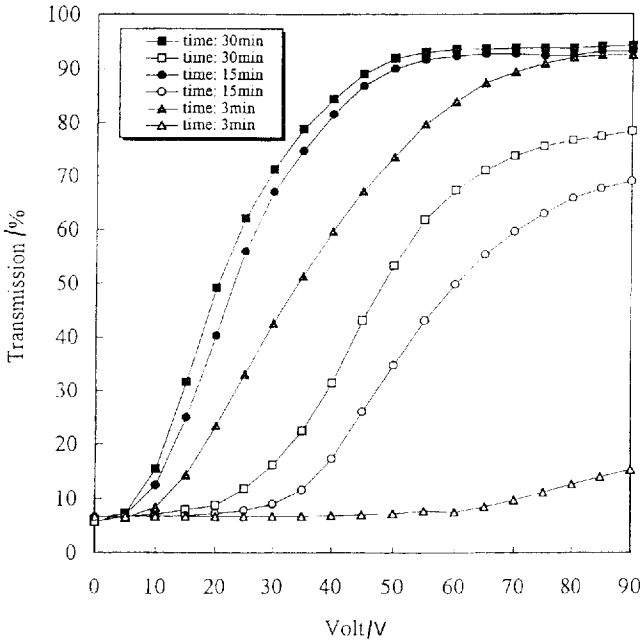
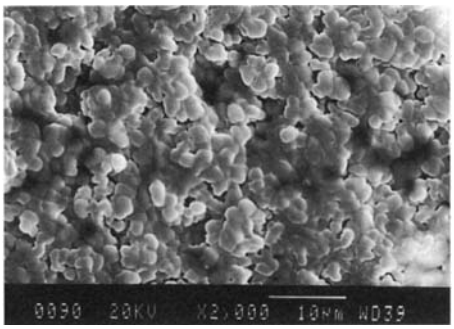


Figure 1. Voltage–transmission property in the ON state (filled symbols) and in the memory state (open symbols) for 'polymer ball' PDLC samples cured with different curing times.

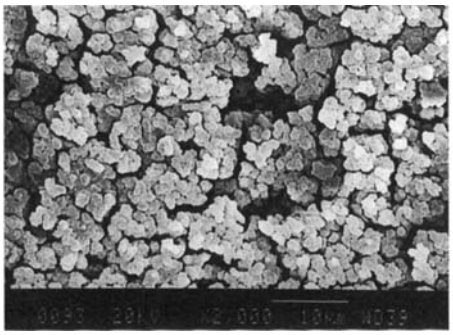
transmission of the resulting PDLC film will become lower. The incomplete polymerization can also be used to explain the poor optical properties of the 3 min cured sample as shown in figure 1.

3.2. *Samples prepared with different curing intensities*

In this experiment, three 'polymer ball' PDLC samples were prepared with E7:K15 = 1:1, HEMA:(E7 + K15) = 1:1, and the photoinitiator (DEAP) concentration was 7·69 % wt. The film thickness was fixed at 12 μm and the samples were cured for 30 min with different curing intensities of 5 mW cm^{-2}, 20 mW cm^{-2} and 40 mW cm^{-2}. Figures 3 (*a*) and (*b*) show the electro-optical characteristics of the three 'polymer ball' PDLC samples. From figures 3 (*a*) and (*b*), we can see that for samples cured at a lower curing intensity, the scattering effect is weaker in the OFF state, and the threshold and saturation voltages are larger. On the other hand, for samples cured at a higher curing intensity, the scattering effect is larger in the OFF state, and the threshold and saturation voltages are lower. Similar to the data shown in figure 1, these results suggest that a weak curing intensity results in an incomplete polymerization. The SEM pictures further confirmed this assertion. Figure 4 (*a*), (*b*) and (*c*) show the SEM pictures of these three samples cured at curing intensities of 5 mW cm^{-2}, 20 mW cm^{-2} and 40 mW cm^{-2}, respectively. These pictures clearly indicate that the curing intensity has a



(*a*)



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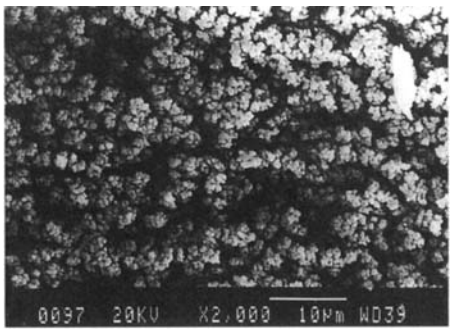
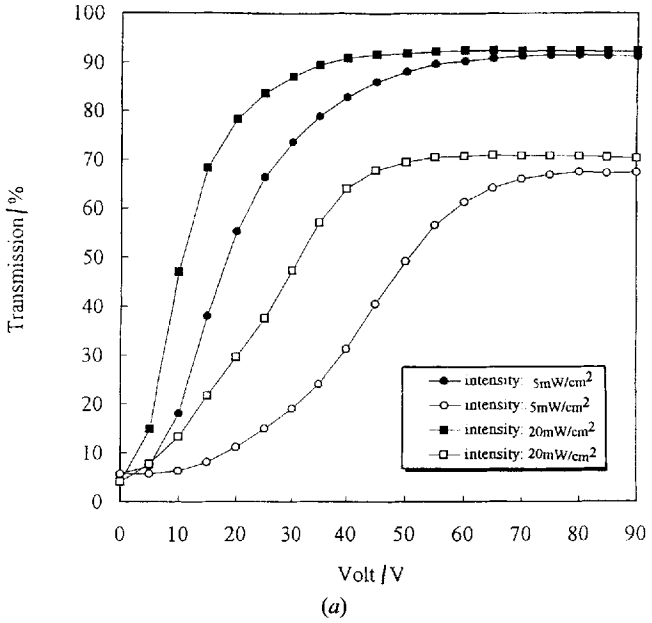
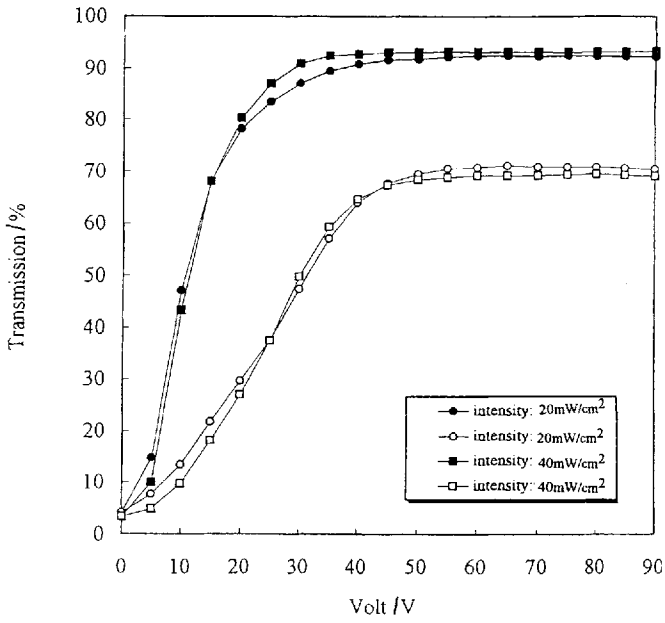


(*c*)

Figure 2. SEM pictures of 'polymer ball' PDLC samples cured with a different curing time of (*a*) 3 min, (*b*) 15 min and (*c*) 30 min.



(*a*)



(*b*)

Figure 3. Voltage–transmission property in the ON state (filled symbols) and in the memory state (open symbols) for 'polymer ball' PDLC samples cured with different curing intensities.

profound effect on the morphology of these samples. Similar to the short curing time effect discussed earlier, a lower curing intensity will also result in an incomplete polymerization, and consequently, the OFF state transmission is higher for samples cured at a lower curing intensity. Also, when the curing intensity is low, the monomer molecules can form larger polymer balls so that the bonding domains that the liquid crystal molecules occupy become smaller. As the domain size becomes smaller, the liquid crystal/polymer interaction becomes more significant. The more 'anchored' the liquid crystal with the polymer ball, a greater field-induced torque will be needed to switch the texture. This manifests itself as an increase in the driving voltage. Thus, samples cured with a smaller curing intensity will have a larger threshold voltage. This is contrary to the 'droplet' PDLC [1] due to the fact that the 'polymer ball' PDLC has a reverse morphology.

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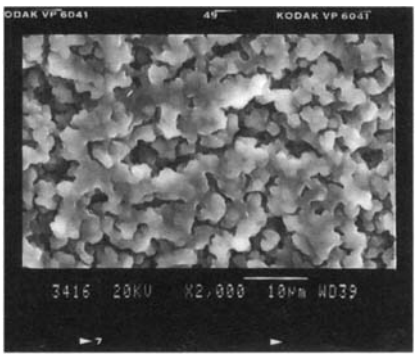
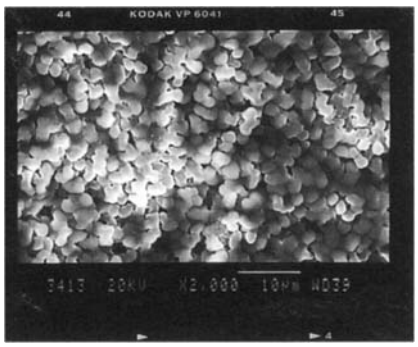


(*a*)



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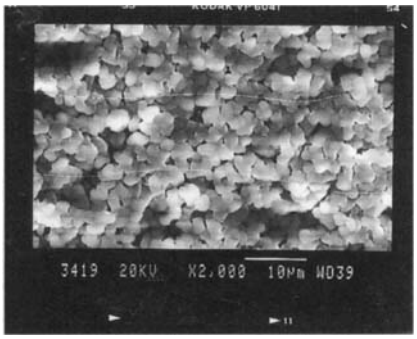
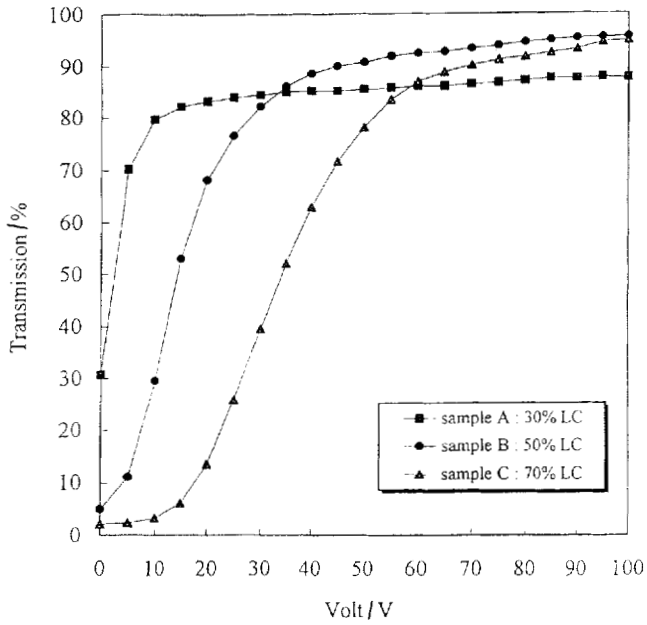


(*c*)

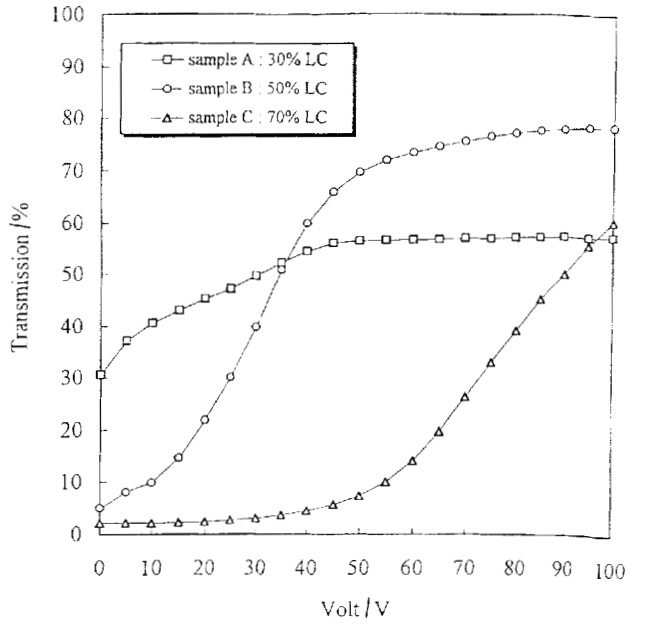
Figure 4. SEM pictures of 'polymer ball' PDLC samples cured with a different curing intensity of (*a*) 5 mW cm^{-2}, (*b*) 20 mW cm^{-2} and (*c*) 40 mW cm^{-2}.

3.3. *Samples prepared with different monomer/liquid crystal ratios*

The ratio of the monomer and liquid crystal is also an important factor in determining the optical properties of 'polymer ball' PDLC films. To understand this effect, three samples with different ratios were prepared as shown in the table. These three samples, with a fixed thickness of 12 μm, were all cured under a curing intensity of 15 mW cm^{-2} for 30 min. Figures 5 (*a*) and (*b*) show the ON state and memory state transmission of these



(*a*)



(*b*)

Figure 5. The (*a*) ON state and (*b*) memory state transmission for samples prepared with different monomer/liquid crystal ratios.

three samples. From figure 5 (*a*) it can be seen that sample A, with a small amount of liquid crystal (30 per cent), has a high OFF state transmission (> 30 per cent). On the other hand, although sample C, with a large amount of liquid crystal (70 per cent), has a small OFF state transmission (< 3 per cent), its threshold and

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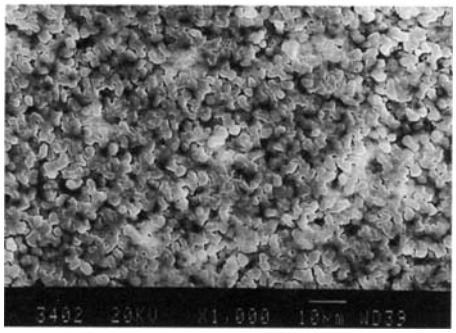
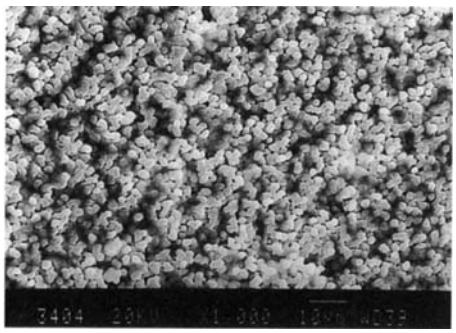
'Polymer ball' PDLC samples prepared with different monomer/liquid crystal ratios.

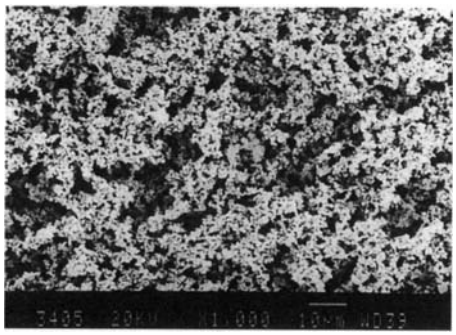
Sample	E7 : K15	HEMA : (E7 + K15)	Photoinitator/per cent
A	1 : 1	7 : 3	5·36
B	1 : 1	1 : 1	5·36
C	1 : 1	3 : 7	5·36



(*a*)



(*b*)



(*c*)

Figure 6. SEM pictures of 'polymer ball' PDLC samples prepared with different monomer/liquid crystal ratios of (*a*) 7:3, (*b*) 1:1 and (*c*) 3:7.

saturation voltages are high. These results suggest that sample B, with a medium amount of liquid crystal, seems to be a better choice for practical applications. We can also reach the same conclusion from the memory state data shown in figure 5 (*b*). The SEM pictures of these samples are shown in figures 6 (*a*), (*b*) and (*c*). From these pictures, we can see that when the amount of monomer is larger (see figure 6 (*a*)), the polymer structure can be clearly observed. However, when the amount of monomer is low (see figure 6 (*c*)), the size of the polymer ball is small and the shape becomes irregular. These observations can also be used to explain why sample C has larger threshold and larger saturation voltages.

4. Summary

In summary, 'reverse' or 'polymer ball' PDLC samples were prepared by the PIPS method. A detailed study of the effects of the sample preparation parameters, such as curing time, curing intensity and liquid crystal concentration, has been reported. It was found that by adjusting these parameters, we can change the morphology of these 'polymer ball' PDLC samples and thus change their optical characteristics. Under incomplete polymerization, the size of the polymer ball is small and results in a poor optical property. Some samples will even lose their memory characteristics. Also, when the amount of monomer is too low, the shape of the resulting polymer ball will become irregular, and the sample will have larger threshold and saturation voltages.

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